NCL 69-11R

EFFECTS OF IMPURITIES ON CARRIER LIFETIME IN BULK SOLAR-CELL MATERIAL

QUARTERLY REPORT

FEBRUARY 1969

Contract No. 952256

NORTHROP CORPORATE LABORATORIES
3401 West Broadway
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NOTICE

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NEW TECHNOLOGY

All technological developments to date are reported herein. They are considered to be unreportable under the instructions of NHB 2170.2 dated October 1966.

ABSTRACT

Studies of lifetime degradation in silicon irradiated with electrons produced by a 2-MeV Febetron reveal that the post-irradiation lifetime is extremely sensitive to the sample surface. Removal of the surface by either etching or lapping changes the lifetime of most samples substantially. Since this behavior is not observed in similar materials following neutron, Co^{60} γ, or 10 MeV electron irradiation, it is presumably due to surface states produced by low energy electrons in the spectrum produced by the Febetron. A further consequence of the low energy spectrum is the nonuniform distribution of damage inside samples and the resulting inconsistent and nonreproducible lifetime degradation of identical samples. To eliminate these effects and thus permit a more valid evaluation of possible impurity effects in various materials, more penetrating Co^{60} γ radiation will be employed in future studies. Results of preliminary studies of gamma-irradiated material indicate that the lifetime damage constants of identical samples are consistent and reproducible while the annealing behavior is dose-dependent. Isochronal annealing studies of electron-irradiated samples indicate that lifetime recovery is influenced by both the dopant and the oxygen concentration. All of the samples studied except one containing boron and grown by the vacuum-float-zone technique (oxygen-free) exhibited abrupt recovery stages above $\sim 200°C$ but little or no gradual recovery at lower temperatures. The recovery stage occurred at a higher temperature in B- and P-doped samples containing high oxygen concentrations than in similarly-doped samples containing less oxygen. A reverse annealing stage beginning at $\sim$ 144°C was observed in the B-doped vacuum-float-zone sample but was not observed in B-doped samples containing moderate to large amounts of oxygen nor in Al-doped samples grown by modified float-zone processes. Similar reverse annealing behavior is

observed in oxygen-free B-doped material irradiated with 10 MeV electrons but is not seen in neutron-irradiated material. Four new crystals are being obtained from the General Electric Company to provide a comparison with similar materials obtained previously from a different supplier. These crystals are expected to be superior to those previously obtained and will be used to investigate impurity effects produced by Co^{60} γ radiation. Several samples have been prepared by diffusing Li into ~ 160 ohm-cm P-doped blanks and will also be γ irradiated.

CONTENTS

INTRODUCTION

This report describes current progress in an experimental investigation of radiation effects in bulk silicon containing non-conventional dopants or excess oxygen concentrations. The purpose of the investigation is to determine whether the damage process involves impurities and, if so, whether the use of certain impurities decreases the radiation sensitivity of the material. Since the minority carrier lifetime is the most radiation-sensitive electrical parameter of both devices and bulk material, this property is being used to monitor the damage produced by types of radiation that are likely to produce impurity-related defects.

TECHNICAL DISCUSSION

LIFETIME DEGRADATION STUDIES

Lifetime damage constants for eighteen samples which were irradiated with electrons from the 2-MeV Febetron were shown in the Second Quarterly Report (November 1968). These results were questionable, however, because of large variations in the damage constants of identical samples and because they indicated that n- and p-type materials were about equal in sensitivity to radiation. The latter result is contrary to common observations that p-type material is significantly more resistant to radiation than n-type. The large scatter in the results was initially attributed to trapping effects, but subsequent experiments revealed that the post-irradiation lifetime and, consequently, the damage constant was strongly influenced by the sample surface. For example, the apparent post-irradiation lifetime of some samples was changed by a factor of five after etching or lapping the surfaces. This result was unexpected for several reasons. First, the surfaces of samples used in these experiments are lapped rather than etched to purposely produce maximum surface effects before irradiation. Since the samples are already in "worst case" condition, effects of surface states introduced during irradiation should be minimized, thus insuring that bulk properties are being measured. A second reason for surprise at the results is the fact that we had not observed surface effects in previous studies of neutron- or 10 MeV electron-irradiated material. Lifetime damage constants determined for identical samples in these previous studies were both consistent and highly reproducible.

Since the spectrum of electrons produced by the 2 MeV Febetron consists of a relatively large number with low energies, the surface effects observed were attributed to a combination of surface states and the non-uniform damage distribution produced by the low energy electrons.

A second group of sixteen samples was irradiated in a subsequent experiment to determine whether more accurate and reproducible lifetime damage constants could be obtained using the Febetron spectrum if samples were etched and lapped after irradiation to remove the more highly damaged surface layer. The experimental techniques employed in this investigation were identical to those used in the previous experiment with the exception that the electron dose was reduced approximately 50% to improve the accuracy of the post-irradiation measurements, and each sample was both etched and lapped immediately before the post-irradiation measurement was performed. Although the results of this second experiment were generally more consistent than those obtained in the first, the data were still not as reproducible or as reliable as desired. Because the more highly damaged surface layer had been removed before the post-irradiation lifetime was measured, it was concluded that the results were due to the non-homogeneous distribution of damage in the samples. Since it is not practical to harden the spectrum by the use of absorbers, it was decided to employ more penetrating Co^{60} γ irradiation in future studies. In addition to producing a homogeneous distribution of damage, the use of a Co^{60} γ source permits the simultaneous irradiation of a large number of samples thus eliminating possible effects due to dosimetry errors. Such a source provides a further advantage that the dose rate more nearly approximates that of a space radiation environment. A lower dose rate is also desirable since it is possible that the surface effects observed in the electron-irradiated material are related to the extremely high dose rate produced by the Febetron.

Seventeen samples were prepared and irradiated simultaneously in the Northrop 5-kci Co^{60} gamma facility at a dose rate of 1.7×10^5 R/Hr. In order to minimize annealing during the relatively long exposure time (72 hrs), the samples were irradiated at dry ice temperature (-78° C) and were kept at this temperature until the post-irradiation lifetime was measured. The experimental results are summarized in Table I which shows the initial and post-irradiation lifetimes and the lifetime damage constant for each sample. Recall that the damage constant, K, is defined through the relationship

$$\frac{1}{\tau} = \frac{1}{\tau_o} + \frac{\phi}{k} \qquad (1)$$

where τ_o and τ are the initial and post-irradiation lifetimes, respectively, and ϕ is the gamma fluence. The damage constant thus indicates the fluence required to reduce the lifetime of an initially perfect sample ($\tau_o \approx \infty$) to 1 μs. As in previous reports on this project, the sample designation scheme employed in the table indicates the crystal manufacturer, growth method, chemical dopant, and the resistivity at room temperature before irradiation. Manufacturers M, D, S, G, T, and K are Merck, Dow, Semi Elements, General Electric, Texas Instruments, and Knapic Electro-Physics, respectively. The vacuum-float-zone, Czochralski or crucible, float-zone in an argon atmosphere and Lopex crystal growth techniques are denoted by the letters V, C, F and L, respectively. Samples designated SCBO and SCPO contained excess oxygen in addition to the normal boron or phosphorus dopants.

As indicated in Table I, the damage constants for similar samples are reasonably consistent and the data further indicate that n-type material is much more sensitive to radiation than is p-type. These results are encouraging and tend to support our interpretation that the

TABLE I

LIFETIME DAMAGE CONSTANTS FOR
Co^{60} γ-IRRADIATED SILICON

Sample Designation	τ_o (μ s)	τ (μ s)	K (photons cm^{-2} μs) 10^{17}
		p-type samples	
MVB 8.3	289	18.7	3.93
MVB 7.9	127	18.8	4.27
DVB 9.9	39.7	14.4	4.47
SCBO 6.8	24.5	9.81	3.22
SCBO 7.0	18.3	9.67	4.01
SCBO 6.3	13.0	7.65	3.64
SCNa 30.5	43.3	12.0	3.28
SCNa 33.7	67.1	16.4	4.27
GFAl 10.1	382	18.2	3.78
GFAl 10.3	476	18.8	3.85
TLAl 6.7	164	5.05	1.02
TLAl 6.7	162	5.05	1.02
TLAl 6.4	123	4.47	0.91
		n-type samples	
KCP 7.9	476	2.23	0.44
KCP 6.0	231	2.16	0.43
SCPO 3.8	24.5	1.01	0.21
SCPO 3.9	21.4	1.08	0.22

inconsistent results obtained for the electron-irradiated samples were due to the nature of the damage and not to our experimental techniques. It should also be mentioned that the post-irradiation lifetimes of these samples were completely independent of the surface condition.

Further examination of the data in Table I reveals that the damage constants of both n- and p-type samples containing excess oxygen concentrations are smaller than those of similarly doped samples which did not contain oxygen as an added impurity. A similar result was observed in samples irradiated with electrons from the 2-MeV Febetron although the difference was not as convincing because of the large variation in the K values of similar samples. In contrast, we have previously found that crucible-grown samples containing up to $\sim 10^{18}$ oxygen atoms cm^{-3} are considerably more resistant to lifetime degradation by 10-MeV electrons than are vacuum-float-zone ("oxygen free") samples containing similar dopants. Additional samples of both types will be irradiated in the future to confirm whether the materials which contain high oxygen concentrations are more sensitive to gamma damage.

In previous studies of neutron-irradiated silicon, we found that crucible-grown Al-doped material was less sensitive to lifetime degradation than were materials containing other dopants.[1] The relatively small damage constants exhibited by all of the Al-doped samples in Table I are consequently unexpected. All of the samples employed in the present study contained low oxygen concentrations, however, and the conflicting results may indicate a dependence upon this impurity in Al-doped material. "Oxygen free" samples have been used because of the higher initial lifetime and appreciably smaller trapping in this material, but lifetime degradation studies will also be performed on crucible-grown samples in the future in an attempt to resolve this conflict.

The large difference in the apparent sensitivity of GFAl and TLAl samples is also surprising since these materials were similar except for minor differences in the dopant concentrations and in the crystal growth techniques. However, the consistency of the results for identical samples indicates that the difference in the damage constants of different crystals is real. These results are typical of the confusion regarding Al-doped material. Evidently an unknown parameter affects this material, and further investigation is merited.

The Na-doped samples used in this experiment had a relatively high resistivity (~ 30 Ω cm) compared to the other materials (~ 4 to 10 Ωcm). Since the damage constant is expected to increase with resistivity, the fact that the K values for these two samples are similar to those of the less pure samples containing other dopants indicates that Na-doped material is not as radiation resistant as material containing more conventional dopants.

ISOCHRONAL ANNEALING STUDIES

A number of samples have been isochronally annealed following electron or Co^{60} γ irradiation to detect possible impurity effects in these materials. Some of these studies were performed earlier and the results were described briefly in previous reports. However, in most cases, the studies have since been extended to higher temperatures or have included different materials and the results are presented here in more detail.

Figure 1 shows the fractional change in the reciprocal lifetime (measured at 30°C) remaining in five samples from the same boron-doped crystal following Co^{60} γ irradiation and 30-minute anneals at the

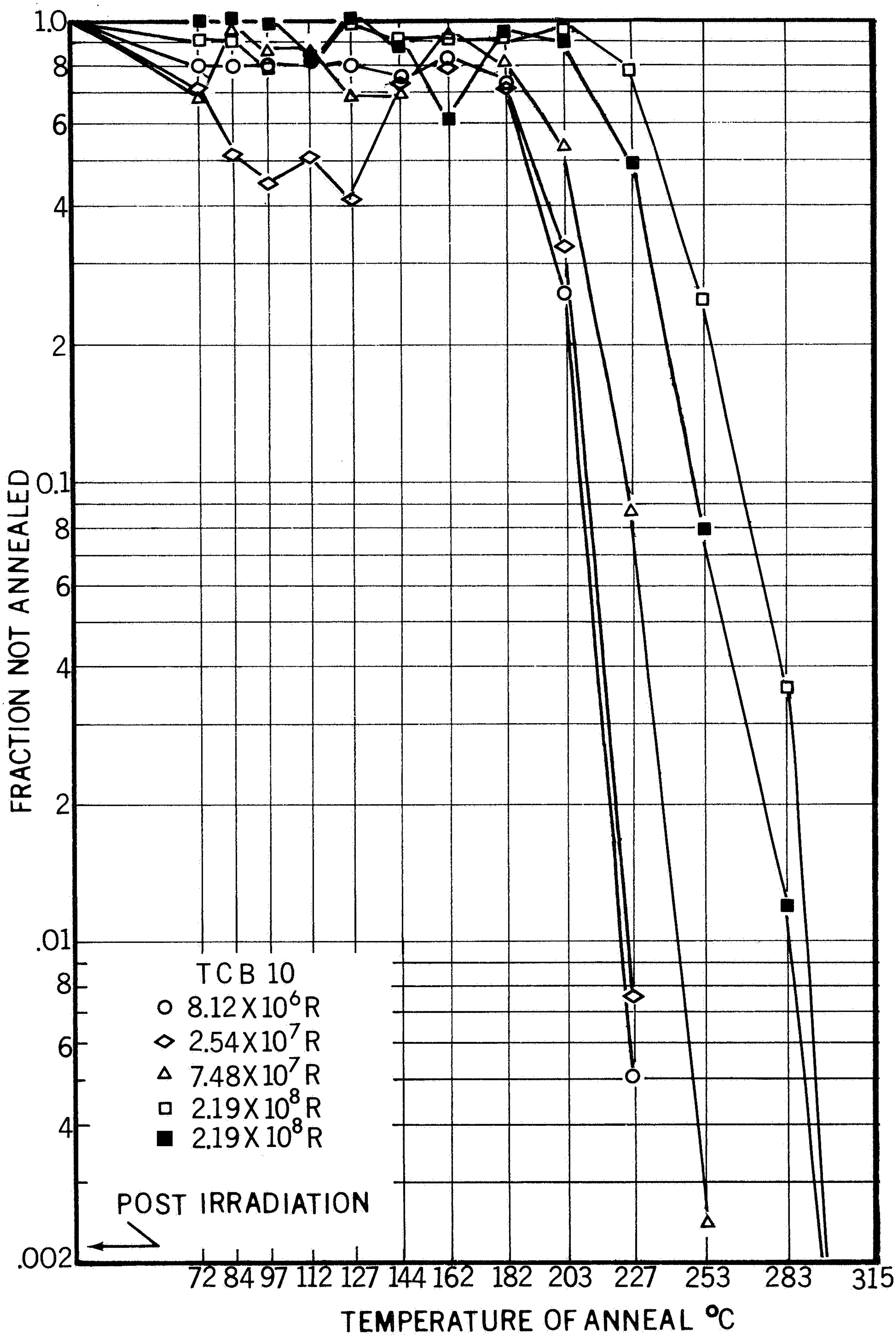

Figure 1. Effect of Dose on Lifetime Recovery in Co^{60} γ-irradiated B-doped Silicon

indicated temperatures. Since the lifetime is expected to vary inversely with the recombination center concentration, the curves represent the fraction of radiation-induced recombination centers remaining after each anneal. The fraction not annealed, f, is defined as

$$f \equiv \frac{\frac{1}{\tau_T} - \frac{1}{\tau_o}}{\frac{1}{\tau_\phi} - \frac{1}{\tau_o}} \qquad (2)$$

where τ_T is the lifetime at the reference temperature (30° C) following an anneal at temperature T, and τ_o and τ_ϕ are the initial and post-irradiation lifetimes at 30° C respectively.

Although there is some variation in the annealing behavior of the samples at lower and intermediate temperatures, the most obvious features of the curves are the rather abrupt recovery stage at high temperature and the fact that the temperature at which it occurs is apparently dose-dependent. Because of this effect, the temperature required to obtain essentially complete recovery increases with increasing dose. The two samples which were exposed to the same dose (2.19×10^8R) also exhibit different recovery rates at high temperature but this difference is believed to be related to the anomalously behavior of one of the samples (represented by the solid squares) during the earlier periods of the irradiation. All of the samples were placed in the gamma source simultaneously and the different doses were obtained by removing samples after given periods. The lifetime of each sample was measured approximately every 24 hours during the first several days and all but the anomalous sample were found to degrade at a similar rate. The latter sample degraded at a much smaller rate initially but the lifetime was similar to that of the other heavily irradiated sample at the end of the irradiation.

As indicated in Figure 1, less than 1% of the lifetime damage remained in any of the samples after the annealing cycle. These same samples were subsequently re-irradiated with a moderate gamma ray dose and were isochronally annealed at the same temperatures used in the previous treatment. All of the samples were irradiated simultaneously and all received an identical dose of 1.40×10^7 R. The isochronal annealing behavior at the higher annealing temperatures is shown in Figure 2. The curves indicate that the amount of damage remaining at the higher temperatures is again dependent upon the dose received in the first irradiation (or the total dose). This apparent "memory" of prior radiation damage is surprising and indicates that one many not obtain significant recovery of devices in a radiation environment by simply heating them to moderate temperatures during off periods. The results also point out the necessity of exposing samples to similar levels of radiation in order to avoid confusing impurity effects with those due to a possible dose dependence.

Nine of the samples which had been previously irradiated with electrons from the 2-MeV Febetron were isochronally annealed to study lifetime recovery in these materials. Annealing curves for these samples are shown in Figures 3 through 5. Except for the fact that the annealing temperatures have been plotted reciprocally, the curves are similar to those shown in the two previous figures. The presence of the abrupt annealing stage at high temperature in all but one of the samples is quite surprising considering our earlier interpretation that the surface dependence of the damage constant and the inconsistency of the values for identical samples was due to inhomogeneous damage distribution. One would expect more gradual recovery beginning at lower temperature in this case.

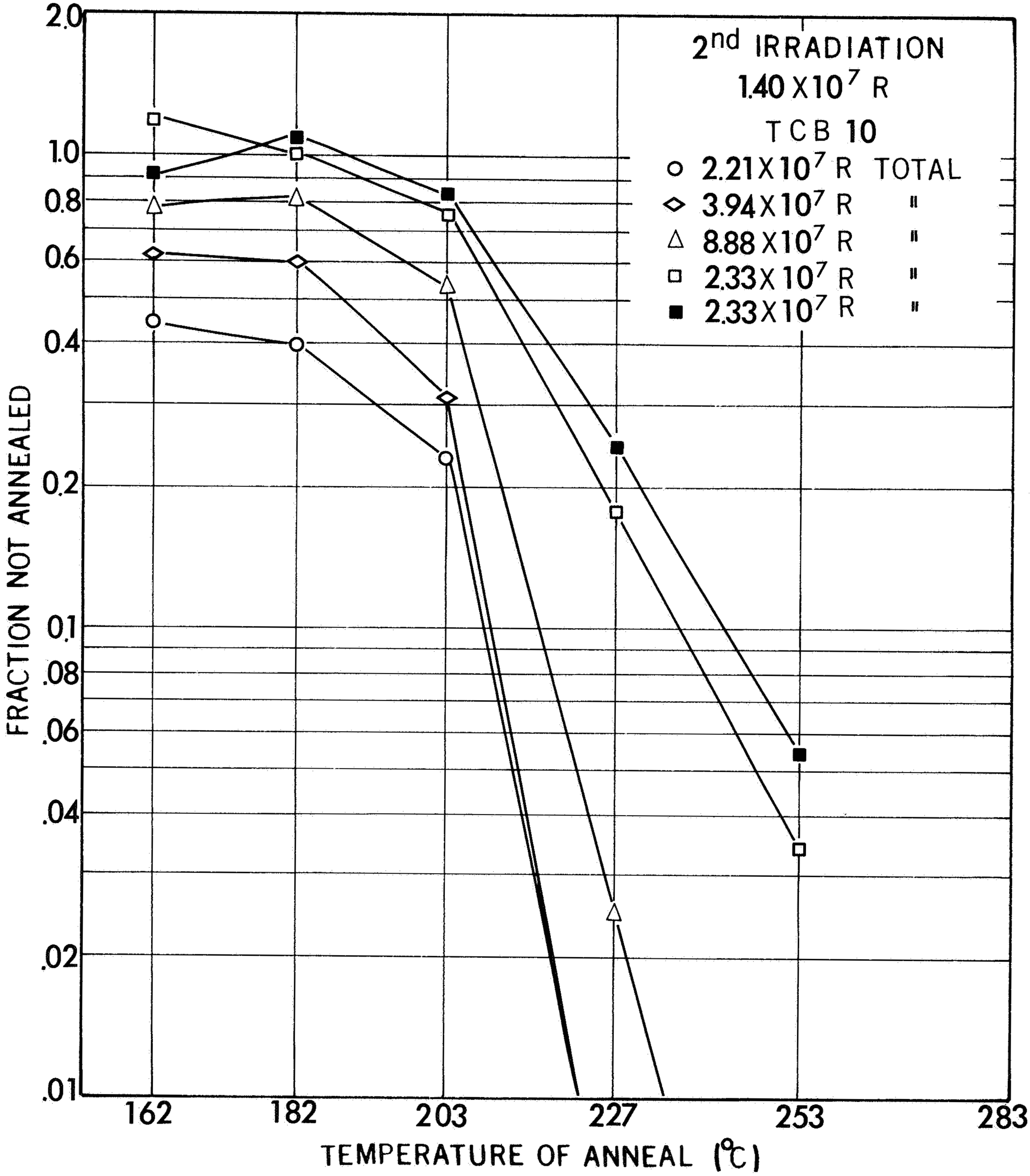

Figure 2 Effect of Prior Radiation History on Lifetime Recovery in Co^{60} γ-irradiated B-doped Silicon

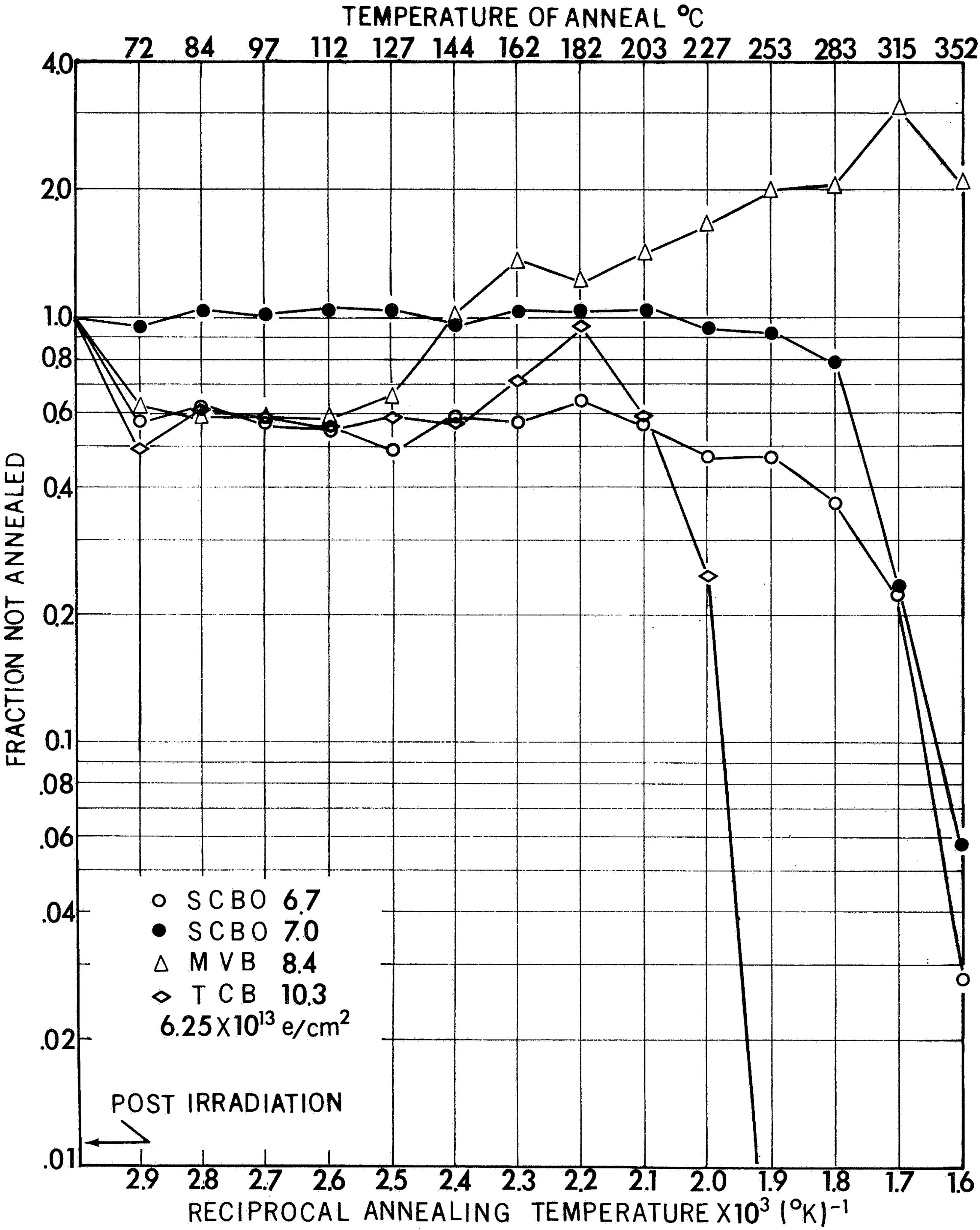

Figure 3 Isochronal Annealing of Reciprocal Lifetime at 30°C in B-doped Silicon Irradiated with 2-MeV Electrons

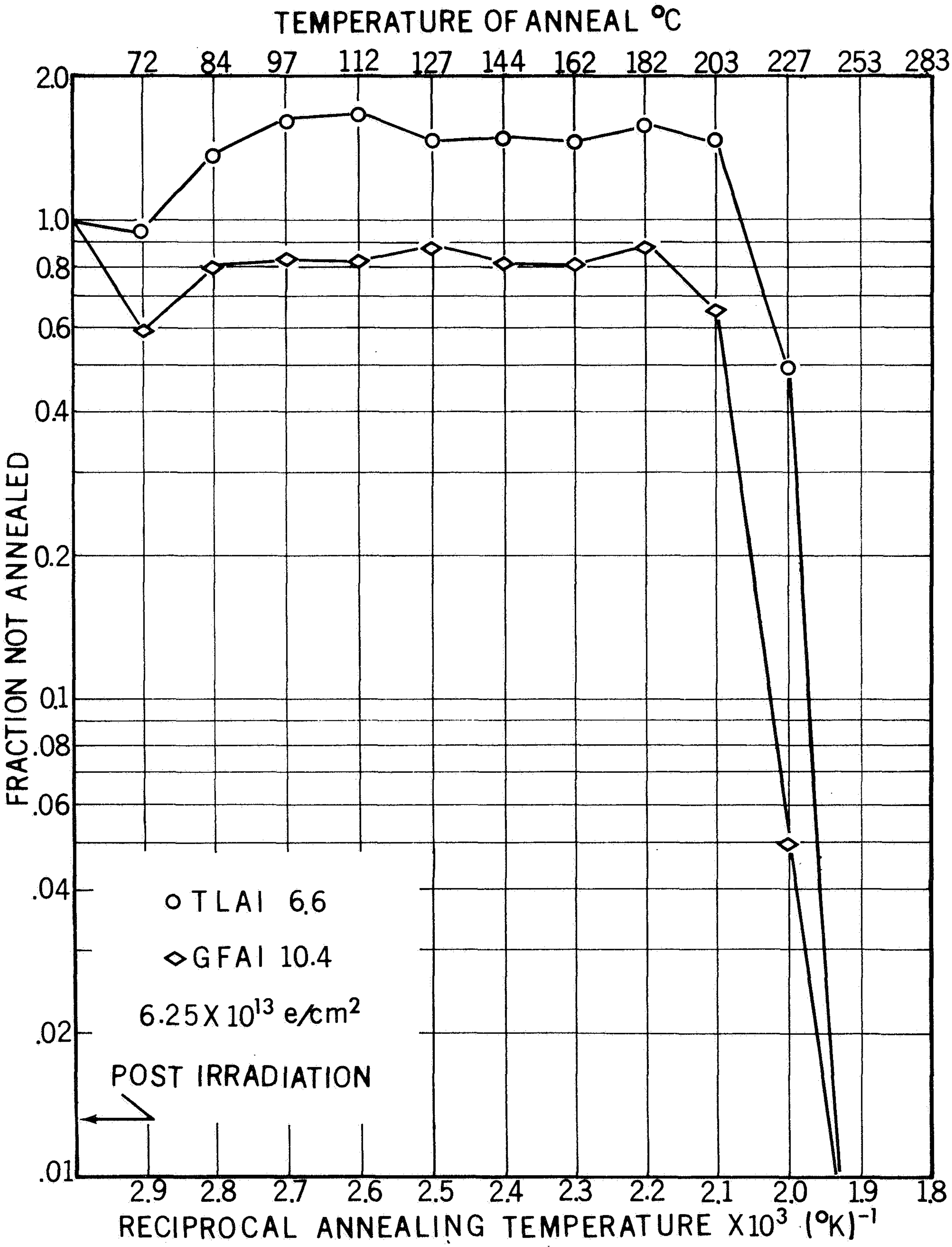

Figure 4 Isochronal Annealing of Reciprocal Lifetime at 30°C in Al-doped Silicon Irradiated with 2-MeV Electrons

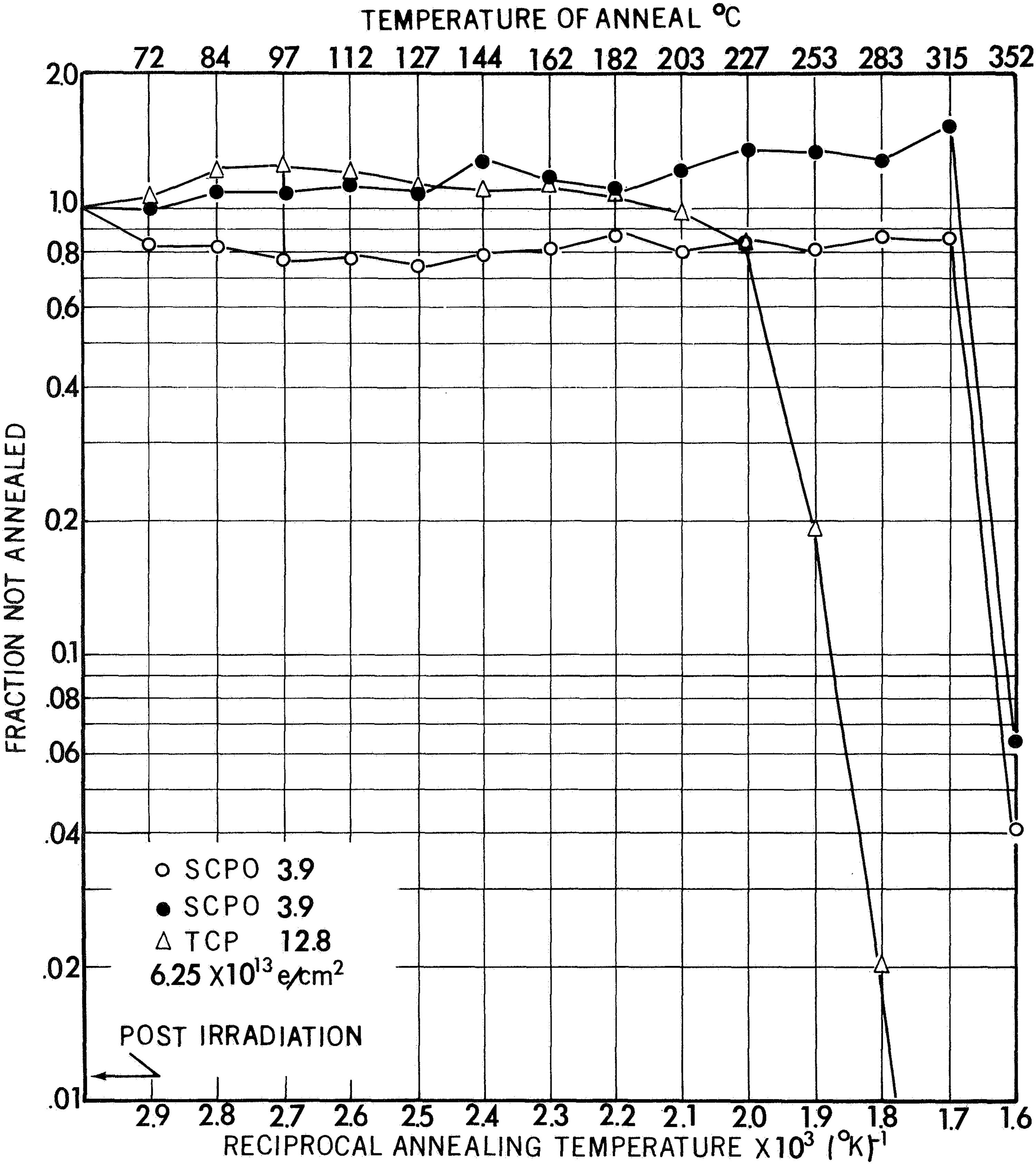

Figure 5 Isochronal Annealing of Reciprocal Lifetime at 30°C in P-doped Silicon Irradiated with 2-MeV Electrons

Figure 3 shows the annealing behavior of three different types of boron-doped samples and reveals that the recovery process in this material is strongly influenced by the crystal growth technique. The crucible-grown control sample (TCB 10.3) recovers at a much lower temperature than the other samples while the "oxygen-free" control sample (MVB 8.4) reverse anneals at $\sim 144°$ C. This sample was subsequently annealed to 636° C and still retained more than 20% of the lifetime damage. A similar reverse annealing stage is observed in B-doped vacuum-float-zone material following irradiation with 10-MeV electrons but is not seen in neutron-irradiated material.[2] The difference in the amount of recovery in the similar SCBO samples at the lower temperatures is not understood. The higher temperature annealing is virtually identical, however.

Figure 4 shows the annealing behavior of two Al-doped samples which were obtained from different sources and which were grown by different float-zone techniques. (The LOPEX technique is a modified float-zone process employed by Texas Instruments, Inc., to produce silicon crystals with low oxygen concentrations and dislocation densities). The curves are very similar in shape and indicate that essentially complete lifetime recovery is obtained in this material at 253° C. Observe that the curves for these "oxygen-free" samples are similar to that of the crucible-grown (Oxygen-containing) boron-doped sample (TCB 10.3) of Figure 3 but are quite different from that of the "oxygen-free" sample (MVB 8.4) which exhibited reverse annealing behavior. Evidently oxygen plays a different role in these materials.

Lifetime recovery is three n-type samples is shown in Figure 5. The crucible-grown control sample (TCP 12.8) recovers at a substantially lower temperature than the two samples which contain oxygen as an added impurity. The curves for the latter samples are also very similar in shape.

LITHIUM DIFFUSION STUDIES

Six lifetime samples have been prepared by evaporating and diffusing Li into blanks made from ~ 160 Ωcm P-doped silicon and employing various subsequent heat treatments. Although the resistivity of this material was reduced to below 5 Ωcm, the lifetime remained greater than 100 μs. Some of the samples will be irradiated with Co^{60} gammas to determine the damage constant for this material and isochronal annealing studies will be performed. Additional samples are being prepared using lithium aluminum hydride as the source of Li to eliminate the evaporation cycle. The use of this material as a Li source was recommended by J. R. Carter of the TRW Systems Group on the basis of experience obtained during an earlier study of the effect of Li in irradiated silicon.[3]

NEW MATERIALS

Four crystals (GCPO, GCBO, GFAl and GFBe employing the sample designation described above) have been purchased from the Semiconductor Products Division of the General Electric Company. All of the crystals have been grown and are in transit at the present. Table II shows the oxygen concentration of each material determined from infrared absorption (9μ) measurements performed by the manufacturer. This organization does not grow silicon crystals for commercial purposes but has demonstrated a very high competence in preparing special crystals for research purposes. The crystals are consequently expected to be superior to those previously used in these studies and should provide more reliable results regarding possible impurity effects in gamma-irradiated material.

TABLE II. OXYGEN CONCENTRATION OF GENERAL ELECTRIC CRYSTALS.

	GCPO	GFAl	GFBe	GCBO
Thickness	0.53 cm	0.50	0.44	0.55
Absorbance at 9 μ	0.77	<0.01	<0.01	0.91
Absorption coefficient	3.3 cm^{-1}	<0.046	<0.052	3.8
Oxygen content	9×10^{17} atoms/cc	$< 1.3 \times 10^{16}$	$< 1.5 \times 10^{16}$	1.1×10^{18}

CONCLUSIONS AND FUTURE PLANS

Studies of lifetime degradation in materials irradiated with electrons from the 2-MeV Febetron have proven inconclusive due to surface effects and inconsistent results. These effects are probably due to the relatively large fraction of low energy (non-penetrating) electrons in the spectrum produced by the machine and are of interest since they do not occur in material irradiated with Co^{60} gamma rays, neutrons, or 10-MeV electrons. However, since these effects prevent an accurate evaluation of possible impurity effects, further studies under this contract will be performed on materials exposed to Co^{60} γ radiation. The effects of this radiation are expected to resemble those produced by low energy electrons except that the damage distribution should be much more uniform in the gamma-irradiated material. Results of a preliminary irradiation support these conclusions and indicate that reliable and consistent results can be obtained. These studies will be extended to include the new materials on order and additional samples from each crystal will be exposed to improve the statistics.

Isochronal annealing studies of electron-irradiated samples indicate that lifetime recovery is influenced by both oxygen and dopant impurities. n- and p-type samples containing excess oxygen concentrations must be annealed at higher temperatures than similarly doped samples which contain less oxygen in order to obtain significant lifetime recovery. This result indicates that the recombination centers involve oxygen or that the defects are trapped at oxygen sites during anneals at moderate temperatures.

Annealing studies have not yet been performed on materials with special dopants following Co^{60} γ-irradiation but such studies will be performed on the crystals supplied by the General Electric Company as well as on samples containing Li after lifetime damage constants have been determined for these materials. Studies of lifetime recovery in identical crucible-grown boron-doped samples exposed to different Co^{60} γ doses reveal that the annealing behavior is dose-dependent. To minimize the effects of this dependence, samples will be exposed to similar doses in future experiments.

REFERENCES

1) Curtis, Bass, and Germano, Report 235-3 For Harry Diamond Laboratories

2) R. F. Bass and O. L. Curtis, Jr., IEEE Trans Nucl. Sci. NS-15, 47 (1968)

3) Private Communication